Progress in heavy-element research: results from relativistic quantum theory

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The production of the heaviest elements was recently marked with new achievements: longer lived isotopes of elements 112 and 114 suitable for chemical investigations were produced in hot-fusion reactions [1]. This allowed for the first successful chemical identification of element 112 as a homolog of Hg with the use of the gas-phase chromatography technique [2,3]. Around the same time, elements 107 and 108 were chemically identified by studying volatility of their compounds with oxygen and chlorine [4,5] using the same approach. New experiments were conducted on aqueous chemistry separations of element 104 [6].

Traditionally, theoretical assistance was rendered to all those important experimental works: detailed predictions of the experimental behavior had been made on the basis of relativistic atomic and molecular calculations, as well as various physico-chemical models. In its turn, the relativistic quantum theory has further developed with respect to the accuracy of the calculated properties, as well as it moved to the description of various new systems of the heaviest elements not yet studied experimentally. Accurate calculations were performed for atoms till Z=122, molecules till Z=118 and very recently for the heaviest atoms interacting with metal clusters with the use of the best available modern quantum-chemical codes. A study of relativistic effects on the electronic structure and properties of these heaviest elements has been an indispensable aspect of those theoretical works. Results of the recent theoretical investigations of the electronic structures and properties of the heaviest elements and their homologs are overviewed in the presentation. A special attention is paid to the predictive power of those theoretical works for chemical experiments.

Atomic calculations. Electronic configurations have accurately been defined for elements up to Z=122 with the use of the Dirac-Fock-Breit Coupled Cluster Single Double excitations (DFB CCSD) method [7]. The multiconfiguration DF (MCDF) calculations for the ground and excited states were performed for elements 104 through 108 [8]. Both types of the calculations have shown that the relativistic stabilization of the 7s electrons of the transactinides results in the stability of the $7s^2$ electron pair in the ground and first ionized state over the entire 7th row of the Periodic Table, which is different from the states of some elements of the 6th row. The relativistic stabilization of the 8p electrons manifests itself in some ground states different than those of the lighter homologs: for example, the $8s^2 8p$ state of element 121 differs from the $8s^2 7d$ state of the lighter group-3 homologues, or the $8s^2 7d 8p$ ground state of element 122 differs from the $7s^2 6d^2$ state of Th. These new DF CCSD results are in agreement with the old single-configuration DF and Dirac-Slater (DS) results of [9].

Ionization potentials (IP) were accurately defined by the DF CCSD calculations for elements up to Z=115, and 119 through 122. Multiple IPs were calculated using the MCDF method for elements 104 through 108 [8]. These calculations have shown the multiple IP to decrease within the transition element groups. The reason for that is the proximity of the relativistic valence 7s and 6d levels. This makes excitation energies of the 6d elements smaller than those of the lighter 4d and 5d homologues, resulting in an enhanced stability of the maximum oxidation states. Due to the same reason lower oxidation states at the beginning of the 6d series will be unstable.

Ionic radii (IR) of elements 104 through 108 have been defined on the basis of the MCDF calculations [8]. The values indicate that for the elements in the maximum oxidation state the IR of the transactinides

are about 0.05 – 0.06 Å larger than the IR of the lighter 5d homologs. The IR of the lighter 6d elements are, however, smaller than the IR of the actinides, since the latter undergo the actinide contraction of 0.030 Å which is mostly a relativistic effect. The calculated radii of the radial charge density R_{max} show that the maximum of the relativistic 7s orbital contraction falls on element 112.

Molecular calculations. Relativistic calculations have by now been performed for all the compounds of the heaviest elements studied experimentally. Two recent works on predictions of the electronic structure and volatility should be mentioned: on MO_3Cl (M=Tc, Re and Bh) [10] and MO_4 (M=Ru, Os and Hs) [11]. In those papers, volatility was predicted for specific gas-phase experiments on the basis of the fully relativistic (four-component) density function theory (DFT) calculations with the use of the physisorption models. It was shown that the volatility of the MO_3Cl species should change as Re > Tc > Bh due to increasing dipole moments in this row. The calculations for the group-8 tetroxides have shown that HsO_4 should be very similar in its electronic structure and properties to OsO_4. On the basis of these calculations using models of physisorption it was predicted that OsO_4 and HsO_4 should have similar adsorption enthalpies on a quartz surface of the chromatography column. Using thermodynamic models of adsorption, the temperature of the deposition of HsO_4 on the quartz surface was predicted to be slightly above that of OsO_4 [12]. Experiments [4] have confirmed the predicted behavior of the group-7 oxychlorides on adsorption, while they disagreed in the T_{ads} for the group-8 tetroxides [5]. The analysis of this disagreement will be given in the talk.

Due to the importance of experiments with element 112, predictions of its experimental behavior have been of a particular value. Early predictions of volatility were made via extrapolations over the lighter homologs in group 12 [13-15]. Predictions of adsorption behavior of element 112 on various metal surfaces from the electronic structure calculations have been of a particular importance. Recently, calculations of intermetallic compounds of element 112 and Hg (HgX and 112X, where X=Cu, Ag, Au, Pd and Pt) were performed using the DFT method [16]. Results of the calculations did not reveal an expected dramatic decrease in the binding energies from the Hg to the 112 compounds. They have shown that element 112 should form compounds with metals like Cu, Ag, Au and particularly Pd, with the bond strength being only 10-15 kJ/mol weaker than that of the respective Hg compounds. Results of the first calculations of adsorption energy of Hg and element 112 on metal clusters of Au and Pd [17] have shown about the same difference in the bond strength between Hg and 112 with gold clusters as that obtained from the dimer calculations [16].

A number of theoretical predictions were made for experiments with aqueous solutions of the heaviest elements. For Rf and its group-4 lighter homologs, predictions of hydrolysis and complex formation in the HF and HCl solutions were made on the basis of the DFT calculations [18]. It was shown that Rf should hydrolyse to a less extent than Zr and Hf. The complex formation in very diluted HF solutions was shown to change as Zr ≥ Hf > Rf, which will result in the following sequence Zr ≤ Hf < Rf by the extraction of the positively charged complexes of these elements by an AIX (anion exchange) column. Experiments [19] on the AIX separation of group-4 elements from HF solutions have confirmed those predictions.

For element 106, Sg, along with Mo and W, predictions of hydrolysis and complex formation in HF solutions were made on the basis of the DFT calculations [20]. Hydrolysis of Sg was shown to be a complex process depending on pH of the solution. At low pH, i.e. for the formation of positively charged complexes, the decreasing trend in hydrolysis of group-6 elements is continued with Sg, so that the trend in the complex formation is Mo > W > Sg. At higher pH, i.e. for the formation of negatively charged complexes, the trend in reversed in the group: Mo > Sg > W. The former trend proved to be in agreement with experiments on the separation of Sg from aqueous HNO_3 solutions by a cation exchange column: Sg having a positive change was sorbed on the column, while the neutral complex of W was not retained [21]. The complex formation of Sg in HF solutions was shown to be even a more complex process than hydrolysis and trends in group 6 were predicted to be different at various pH and HF concentrations.

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Much attention was paid to the study of relativistic effects on the properties of the elements at the end of the 6d-series and at the 7p-series. A series of calculations using the relativistic pseudo-potential (PP) method was performed for compounds of elements 111 through 114 which are expected to have strong relativistic effects on their properties [22]. Energies of decomposition reactions of hydrides, fluorides and some chlorides of those elements were calculated. A most important conclusion of those works is that the relativistic stabilization and contraction of the 7s orbital in the 7th row results in the smallest bond lengths of the 111X and 112X compounds in groups 11 and 12, respectively. On the other hand, relativistic destabilization of the 6d orbitals leads to their larger involvement in bonding for high-coordination compounds, so that the stability of higher oxidation states increases in those groups, like for example of the 5+ state of element 111, or of the 4+ state of element 112. The calculations for the decomposition reactions of the 112 compounds have confirmed its inertness.

Molecular calculations with the use of the relativistic effective core potentials (RECP) for a series of hydrides of the 7p elements [23] have demonstrated a large influence of the 7p orbital spin-orbital (SO) splitting on molecular spectroscopic properties. A large bond contraction was observed in the compounds of element 113 with the predominant contribution of the relativistically contracted $7p_{1/2}$ orbital in bonding (for example in 113H), while for compounds of the other 7p elements, e.g. 115 through 118, the properties are influenced by a relativistically expanded $7p_{3/2}$ orbital. This results in an increase in the bond length of compounds of these elements. The calculations have confirmed a relative inertness of element 114 showing decreasing binding energies of compounds like 114X (X=F, Cl, Br, I, O, O_2) [24] in comparison with those of the lighter homologs. The PP calculations of the decomposition reactions of MX_4 and MX_2 (X=H, F, Cl) have shown a decreasing stability of the 4+ state and increasing stability of the 2+ state for element 114 [22].

The RECP calculations for the reactions $M + F_2 \rightarrow MF_2$ and $MF_2 + F_2 \rightarrow MF_4$, where M=Xe, Rn and element 118 [25] confirmed an increase in the stabilities of the 2+ and 4+ oxidation states in group 18. The SO effects were shown to stabilize $118F_4$ by a significant amount of about 2 eV, though they elongate the bond by 0.05 Å. Thus, increasing trends in bond length and bond strength are continued with element 118. The influence of the SO interaction on the geometry of MF_4 was also investigated [25,26]. It was shown that a D_{4h} geometrical configuration for XeF_4 and for RnF_4 becomes slightly unstable for $118F_4$. A T_d configuration was shown to be more stable than the D_{4h} in $118F_4$ by about 0.2 eV. The reason for that was the availability of only stereochemically active $7p_{3/2}$ electrons for bonding. Trends in molecular stability were predicted for a number of simple compounds of element 118 as compared to those of elements 112 and 114, as well as to those of Rn. So far, elements heavier than 118 were not studied at the MO level. For a complete review, the following references can be recommended [23,27-29]. Prospects for future theoretical studies are also presented in the talk.

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